

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 408 771 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: 90902696.5

(51) Int. Cl.⁵: **C04B 35/10, B24D 3/00,
C09K 3/14**

(22) Date of filing: 01.02.90

(96) International application number:
PCT/JP90/00124

(67) International publication number:
WO 90/08744 (09.08.90 90/19)

(30) Priority: 01.02.89 JP 23010/89

(43) Date of publication of application:
23.01.91 Bulletin 91/04

(64) Designated Contracting States:
AT DE FR GB

(71) Applicant: **SHOWA DENKO KABUSHIKI
KAISHA**
13-9, Shiba Daimon 1-chome
Minato-ku, Tokyo 105(JP)

(72) Inventor: **HATANAKA, Tetsuo Showa Denko
Kabushiki Kaisha**
Shiojiri Research Laboratory 1, Ohaza Souga
Shiojiri-shi Nagano-ken 399-64(JP)
Inventor: **HIRAIWA, Tadashi Showa Denko
Kabushiki Kaisha**
Shiojiri Research Laboratory 1, Ohaza Souga
Shiojiri-shi Nagano-ken 399-64(JP)
Inventor: **MATSUKURA, Minoru Showa Denko
Kabushiki Kaisha**
Shiojiri Research Laboratory 1, Ohaza Souga
Shiojiri-shi Nagano-ken 399-64(JP)
Inventor: **AOKI, Norimichi Showa Denko
Kabushiki Kaisha**
Shiojiri Research Laboratory 1, Ohaza Souga
Shiojiri-shi Nagano-ken 399-64(JP)
Inventor: **IMAI, Shoichi Showa Denko
Kabushiki Kaisha**
Shiojiri Research Laboratory 1, Ohaza Souga
Shiojiri-shi Nagano-ken 399-64(JP)

(74) Representative: **Hansen, Bernd, Dr.**
Dipl.-Chem. et al
Hoffmann, Eitle & Partner Patent- und
Rechtsanwälte Arabellastrasse 4e 4
D-8000 München 81(DE)

EP 0 408 771 A1

(54) **ALUMINA CERAMIC, ABRASIVE MATERIAL, AND PRODUCTION THEREOF.**

TITLE MODIFIED
see front page

SPECIFICATION

ALUMINA-BASED CERAMICS MATERIALS, ABRASIVE MATERIALS
AND
METHOD FOR THE MANUFACTURE OF THE SAME

TECHNICAL FIELD

The present invention relates to improved alumina-based sintered ceramics materials which are made of ultrafine crystals produced by a sol-gel method and has a high hardness and a high density, and to abrasive materials such as abrasive grains, grinding wheels, coated abrasives as well as to their manufacture.

BACKGROUND ART

Manufacture of high-density, alumina (Al_2O_3)-based polycrystalline sintered ceramics abrasive grains by a sol-gel method is known. Japanese Patent Publication JP-A-56-32369 discloses gelation of alumina monohydrate together with a precursor or precursors of at least one reforming component followed by dehydration and drying as well as sintering. The reforming component used in this case includes oxides of Co, Hf, Mg, Ni, Zn, and Zr. Japanese Patent Publication JP-A-60-231462 describes a method for the manufacture of alumina sol/gel in which increase of density of alumina is promoted by the addition of α -alumina seed crystals, and also that a crystal growth control agent

by the method disclosed in Japanese Patent Publication JP-A-60-231462.

DISCLOSURE OF INVENTION

An object of the present invention is to provide a ceramics material having a density equal to or higher than that of conventional α -alumina-based ceramics material and having a fine crystalline structure of an average particle diameter of no greater than 0.2 μm and a method for the production of the same.

Keeping an eye on the fact that abrasive grains composed of a fine crystalline structure exhibit excellent grindability, the present inventors have made intensive investigation with an expectation that the finer the crystalline structure is, the more grindability increases, and as a result they have completed the present invention.

The present inventors studied on influences which the size of crystals of a sintered material might have on the strength of alumina-based sintered ceramics material and performance of abrasive grains made of it. As a result they have found that in the case where the material has characteristics, i.e., a density of no lower than 95% of the theoretical density and a Vickers hardness of no lower than 2,000 kg/mm^2 , the strength of the ceramics material and the performances of abrasive grains made of it are increased to extremely high levels when the crystal size of

containing fine α -alumina crystal grains, heating the gelled product with setting up a maximum temperature in a range of from 1,100 to 1,300°C, time of temperature elevation from 900 to 1,100°C on this occasion being set up to no longer than 90 seconds, retaining the product at a temperature in a range of from 1,100 to 1,300°C for from 30 seconds to 10 minutes and further retaining it at a temperature of from 1,000 to 1,200°C for 1 to 100 hours.

The abrasive grains of the present invention, either in the form of a vitrified grinding wheel or an coated abrasive, exhibit an increased strength or the like of crystals of the abrasive grains and an increased toughness of the abrasive grains as compared with conventional alumina-based sintered abrasive grains by making the crystal size no greater than 0.2 μm on an average or substantially no greater than 0.2 μm and making the crystal size uniform. As for the grindability, the abrasive grains of the present invention exhibit critical values, more specifically, by about twice when they are in the form of a vitrified grinding wheel or by about six times when they are in the form of an coated abrasive as high as the conventional highest quality alumina-based sintered abrasive grains.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a graph showing crystal particle diameter distributions obtained by measurements according to Example

than 0.2 μm on an average or a crystal size of substantially no greater than 0.2 μm .

(Pseudo)boehmite such as SB Pural Alumina commercially available from Condea Co. is at first converted into a sol and fine α -alumina grain having a particle diameter of no greater than 0.2 μm , preferably no greater than 0.1 μm are mixed in the sol so that it can serve as a phase transformation accelerator at the time of calcination and sintering. The fine α -alumina grain which serves as a phase transformation accelerator is capable of decreasing the transition energy from a γ -form alumina to an α -form alumina upon the calcination of a gel formed by drying or the like of the sol, thereby allowing α -conversion to proceed at a low temperature, and at the same time producing a dense sintered material having a high density without causing the crystal size to grow at the time of sintering.

A method of mixing the phase transformation accelerator may be a milling treatment in which a sol or gel is treated using a ball mill, an vibratory ball mill or the like, a method in which powdery fragments of alumina balls formed by abrasion thereof as a result of idle grinding of a ball mill or the like are mixed with an alumina sol or gel, or a method in which fine powder obtained by further milling commercially available fine α -alumina powder is mixed with an alumina sol or gel.

As for the method for the addition and mixing of the above-described oxides, precursors and salts thereof with the alumina sol or gel, a method in which an in-line mixer is used can be used besides a method using stirring. A preferred method is ball mill mixing, and in addition the use of alumina balls on this occasion is advantageous because powdery fragments of α -alumina produced as a result of abrasion of the balls themselves are mixed and the mixing is carried out sufficiently. Particularly, when the above elements are added in the form of salts, mixing cannot be performed sufficiently for achieving uniform addition and mixing unless a ball mill or vibratory ball mill is used because the alumina sol is gelled.

In addition, the above-described precursors mean alkoxides or intermediate products and the like formed during conversion to oxides. As for the salts of the precursors, there can be used nitrates, chlorides, carbonates, acetates, sulfides and the like.

After stirring sufficiently for from 1 to 4 hours in the case of the alumina sol containing a fine α -alumina grain, or after stirring sufficiently in the case where the alumina sol has been gelled, it is slowly dried at a temperature of from 80 to 120°C for from 10 to 72 hours. The reason why it is dried slowly is that while the sol is gelled by drying, including cases where the sol has been gelled before drying, air bubbles contained in the gel is to be removed sufficiently to render the density higher.

rapidly and accelerates rendering the density higher and increases its hardness.

According to the method of the present invention, the alumina gel is subjected to the rapid heat treatment for the above-described temperature range and the maximum temperature is set up at from 1,100 to 1,300°C, and thereafter, retained at a temperature of from 1,000 to 1,300°C. The retention time at this temperature is shorter the higher the temperature is, and is suitably about 30 seconds at 1,300°C and about 100 hours at 1,000°C. Preferred retention time is from 30 seconds to 10 minutes in the case where the retention temperature is in a range of from 1,200 to 1,300°C, and from 10 minutes to 10 hours in the case where the retention temperature is in a range of from 1,100 to 1,200°C, and from 10 to 100 hours in the case where the retention temperature is in a range of from 1,000 to 1,100°C. A more preferred heat treatment method is a two-step sintering method such as the one which includes retention at a temperature in a range of from 1,100 to 1,300°C for from 30 seconds to 10 minutes followed by further retention at a temperature of from 1,000 to 1,200°C for from 1 to 100 hours. This method gives a crystal size of substantially no greater than 0.2 μm , and a uniform crystal size as well as a high hardness.

According to the methods, a ceramics material can be obtained whose crystal size is no greater than 0.2 μm on an average or substantially no greater than 0.2 μm , and which

low temperature range such that the crystal size does not grow extremely (second step).

Actually, an electron micrograph (Fig. 2) of crystal grains of the abrasive grain obtained according to Example 5 described later on shows that not only the crystal size is uniform but also the shape of the crystals is uniform.

While the amount of the phase transformation accelerator used in the present invention is from 1 to 8 wt%, preferably from 1.5 to 3.5 wt% based on the weight of the (pseudo)boehmite in terms of Al_2O_3 , as described above, it is preferred to elevate the temperature of sintering when the amount is large. This is because when the amount is large, the sintering property is aggravated, resulting in that the density and hardness do not increase; when it is added in an amount of no less than 3.5 wt%, the temperature of sintering must be elevated by from 20°C to 50°C.

As described above, it is by the present invention that a ceramics material or abrasive grain having a crystal size of no greater than 0.2 μm on an average or substantially no greater than 0.2 μm , and having a density of no lower than 95% of the theoretical density and a Vickers hardness of no lower than 2,000 kg/mm^2 that has not hitherto been produced can be produced for the first time, and furthermore, increase of the strength upon actual use is achieved because the crystal size is very small and uniform. Particularly, in the case of abrasive grains,

1,150°C lest the crystal size of the abrasive grain should become coarse.

Coated abrasives are produced by bonding a backing and the abrasive grain with an adhesive. As the adhesive, a phenol resin-based adhesive is mostly used in view of excellent grinding characteristics and water resistance. Simultaneous use of resorcinol or its derivatives can alleviate its curing conditions.

As for the backing, there can be cited, for example, paper, woven fabric, and non-woven fabric.

EXAMPLES

Hereafter, the present invention will be explained in detail with reference to examples.

Examples 1 to 4

Two hundred grams (200 g) of (pseudo)boehmite such as SB Pural Alumina marketed by Condea Co. and 1.5 liters of water were mixed in a beaker. Next, to produce a sol, 0.3 liter of 3.6 wt% HNO_3 was added to adjust pH to 2. Then 7 kg of alumina balls and 1.5 liters of water were put into a 7.3-liter alumina pot, and milling was performed in a state of idle grinding for 96 hours to produce a slurry containing mainly powdery fragments formed as a result of abrasion of the alumina balls. The specific surface area of the powdery fragments was $75 \text{ m}^2/\text{g}$.

Next, the slurry containing the powdery fragments was added to the alumina sol prepared as above in such an

The crystal size of the sintered particles, i.e., abrasive grain, was from 0.2 to 0.5 μm and 0.3 μm on an average; the Vickers hardness at a load of 500 g was 2,230 kg/mm^2 ; and the density was 3.89 g/cm^3 , i.e., 98% of the theoretical density.

On the other hand, as will be apparent from Table 1, the abrasive grains of Examples 1 to 4 each had a Vickers hardness of no lower than 2,000 kg/mm^2 and a density at least equal to that of the abrasive grain of Comparative Example 1. In addition, they were fine, having an average particle diameter of no greater than 0.2 μm .

Table 1

		Vickers		<u>Crystal Size</u>	
<u>(μm)</u>		Hardness	Density	Average	
Sample		Hv ₅₀₀ (kg/mm^2)	(g/cm^3)	Particle Diameter	Range
Example 1	After 1st	1,340	3.12	0.08	0.03 ~
0.12	sintering				
	After 2nd	2,120	3.89	0.18	0.05 ~
0.20	sintering				
Example 2	After 1st	1,490	3.58	0.12	0.07 ~
0.15	sintering				
	After 2nd	2,140	3.90	0.18	0.10 ~
0.22	sintering				

Particle diameter data were obtained on 473 and 452 crystal grains, respectively, of the abrasive grains of Example 2 and Comparative Example 1.

The abrasive grain of Example 2 had an average particle diameter of $0.176\text{ }\mu\text{m}$ with a standard deviation of 0.028 . On the other hand, the abrasive grain of Comparative Example 1 had an average particle diameter of $0.309\text{ }\mu\text{m}$ with a standard deviation of 0.077 .

Fig. 1 illustrates a crystal particle diameter distribution. As will be apparent from Fig. 1 and the standard deviation, the abrasive grain of Example 2, the present invention, had a particle diameter substantially no greater than $0.2\text{ }\mu\text{m}$ and thus had a uniform crystal particle diameter.

When the maximum temperature was set up at no lower than $1,300^{\circ}\text{C}$, the growth of grains was promoted so that grains with high growth rates had particle diameters of no smaller than $0.5\text{ }\mu\text{m}$, which makes the distribution of particle diameter broader. In the case of the the particle diameter distribution of the crystals of the abrasive grain obtained in Comparative Example 1, those grains having a particle diameter of no smaller than $0.5\text{ }\mu\text{m}$ occupied about 2% while in Example 2, there was observed no grain that had a particle diameter of no smaller than $0.3\text{ }\mu\text{m}$.

Fig. 2 is electron micrographs of crystal grains of the abrasive grain. From this it can be seen that the abrasive grain of Example 2 had not only a uniform particle

used then had a specific surface area of $112 \text{ m}^2/\text{g}$. The sol thus obtained was transferred to a stainless steel vat and dried for a total time of 48 hours, more specifically at 100°C for 24 hours and then at 120°C for 24 hours, to obtain a gel. After completion of the drying, the gel was crushed with a roll breaker and sieved with a sieve so as to have a particle diameter of from 500 to $350 \mu\text{m}$. The particles were calcined at 750°C for 1 hour to remove moisture and NO_x .

The temperature of the particles were raised to two levels of calcination temperature, i.e., $1,250^\circ\text{C}$ and $1,300^\circ\text{C}$, in 60 seconds and kept at the respective temperatures for 1 minute, followed by heating at $1,100^\circ\text{C}$ for 40 hours.

Table 2 shows the Vickers hardness, density and crystal size of each abrasive grain.

Examples 10 and 11

A boehmite sol was prepared in the same manner as in Examples 1 to 4, and then $\text{Mg}(\text{NO}) \cdot 6\text{H}_2\text{O}$ was added thereto so that MgO was contained in an amount of 0.7 wt% based on the weight of Al_2O_3 . Thereafter, a slurry of powdery fragments was added thereto in the same manner as in Examples 1 to 4, and the mixture was dried to obtain a gel, which was sieved to a particle diameter of from 500 to $350 \mu\text{m}$ and calcined at 750°C for 1 hour. Then, the temperature was raised in 60 seconds from room temperature to $1,150^\circ\text{C}$ and kept at $1,150^\circ\text{C}$ for 10 hours and further treated at $1,100^\circ\text{C}$ and

	Time for elevating temperature from 900 to 1,100°C (seconds)	Vickers Hardness Hv ₅₀₀ (kg/mm ²)	Density (g/cm ³)	Crystal size: Average particle size (μm)
Example 12	30	2,360	3.90	0.2
Example 13	80	2,180	3.85	0.2
Comparative Example 12	120	1,750	3.76	0.2
Comparative Example 12	600	1,380	3.12	0.3

γ -Alumina prepared by removing water and NO_x from alumina-based gel containing from 1 to 8 wt% of fine grains of α -Al₂O₃ is transformed to α -Al₂O₃ at from 900 to 1,100°C. By rendering the range of transformation temperature steeper or rendering the transformation time within 90 seconds as will be understood from Table 3, more sites of formation of α -Al₂O₃ nuclei are obtained, resulting in that the particle diameter of crystals becomes smaller and densities of the grains become higher.

Examples 14 and 15 and Comparative Examples 5 and 6

The abrasive grain after the first step sintering prepared in Example 1 was heated at 900°C, 1,000°C, 1,200°C and 1,350°C, respectively, for from 1 to 100 hours as shown in Table 4, and the results obtained are shown in Table 4.

Table 4

hours. Table 5 shows results of measurements on the Vickers hardness, density and particle diameter of each grain product.

Table 5					
<u>Sintering</u> <u>1,300°C</u> <u>hours</u>	Only	<u>Conditions of Second-Step</u>			
	sintering at 1,050°C	1,150°C 100 hrs	1,250°C		
			1 hour	10 hrs	0.5 hr 2
Vickers hardness 2,030 HV500 (kg/mm ²)	280	800	1,460	1,950	1,880
Density 3.85 (g/cm ³)	2.80	3.10	3.70	3.80	3.81
Crystal size: Average Particle 0.26 diameter (μm)	<0.05	0.15	0.20	0.23	0.22
Comp.	Comp.	Comp.	Comp.	Comp.	Comp.
Ex. 12	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11

As will be understood from Table 5, if the sintering temperature in the first step is below 1,100°C, increases of density and hardness are insufficient and the density

decreased. Table 6 shows the characteristics of the respective abrasive grains.

Table 6

	Comp.	Comp.	Comp.	Comp.	Example
Comp.	<u>Ex. 14</u>	<u>Ex. 15</u>	<u>Ex. 16</u>	<u>Ex. 17</u>	<u>16</u>
<u>Ex. 18</u>					
Tempera- ture (°C) 1,350	1,050	1,150	1,200	1,250	1,300
Vickers hardness 2,120 (kg/mm ²)	< 200	480	1,220	1,980	2,030
Density (g/cm ³) 3.83	2.30	2.90	3.05	3.78	3.80
Crystal Size (μm) 0.24	<0.05	<0.05	0.07	0.13	0.18

The results of Comparative Example 13 in Table 6 indicate that 1,350°C is unsuitable for the maximum temperature for sintering.

Examples 17 to 20

#60 Abrasive grains (100 parts) of Example 3, 4, 8 or 11 were each mixed with 13 parts of borosilicate frit serving as a bond for vitrified grinding wheels, 12 parts of dextrin and 2.5 parts of water using a mixer. The borosilicate frit used was composed of 70% SiO₂, 7% Al₂O₃, 18% B₂O₃, 4% Na₂O + K₂O, and 0.5% CaO + MgO.

Work: SDK-1 (HRC 60) L100 x b50 x t10
 Grinding wheel surface speed: 2,000 m/min
 Table speed: 20 m/min
 Cut-in size: ΔR_{20} $\mu\text{m/pass}$
 Total cut-in size: 5 mm
 Grinding width: 10 mm
 Spark-out: 1 pass
 Grinding oil: Dry type (no oil used)
 Dressing condition: Single stone diamond dresser
 Cut-in: ΔR_{20} $\mu\text{m/pass}$
 Lead: 0.2 mm/r.o.w
 Spark-out: None

As a result, values shown in Table 8 were obtained for the grinding ratio, maximum electric power consumption (value excluding no-load power (0.4 kW)), and surface roughness.

Table 8

	Grinding	Maximum Electric	Surface
Roughness			
Sample	Ratio	Power Consumption	(μRZ)
<u>No.</u>	<u>(mm^3/mm^3)</u>	<u>(KW/cm)</u>	<u>l = 2.5 mm, N =</u>
3			
Example 17	58	1.2	14

Examples 22 to 24

Resorcinol (10 parts) was dissolved in 10 parts of ethanol, and the resulting solution was mixed with 100 parts of one of three abrasive grains of Examples 3, 4 and 8. The mixture was dried at 100°C for 1 hour to remove ethanol by evaporation. As a result, three kinds of abrasive materials whose surfaces were coated with resorcinol were obtained.

The phenol resin bond BRL-2867 (about 70 wt% solid, product by Showa Kobunshi Co.) was evenly coated on a compressed non-woven fabric base material at a coverage of 100 g/m², and then the coated abrasive materials were spread out and excess abrasive material was removed. The three kinds of abrasive materials were deposited on the base material each in an amount of 250/m². These sheets were dried at 80°C for 4 hours, and thereafter the bond was coated evenly in a proportion of 200 g/m², and then dried at 80°C for 4 hours. The temperature was then raised from 80°C to 135°C in 2 hours, retained at 135°C for 30 minutes, and three kinds of coated abrasives were thus obtained.

Comparative Example 21

In relation to the abrasive grain of Comparative Example 1, coated abrasives with a non-woven fabric base material were produced in the same manner as in Examples 22 to 24.

Table 11 Grinding of SUS-304

<u>Sample No.</u>	<u>Initial Grinding Amount (g/min)</u>	<u>9-10 Minutes Grinding Amount (g/min)</u>	<u>Total Grinding Amount (g)</u>
Example 22	6.1	2.5	33.7
Example 23	5.1	2.8	35.3
Example 24	5.6	2.5	33.3
Comparative Example 21	4.9	-	6.2

The reason why Table 11 lacks figures for 9-10 minute grinding amounts in Comparative Example 21 is that the materials to be ground started a burn in 4 minutes, the ground amount had fallen to an extremely low value, and the grinding therefore had to be stopped.

The performances of the products of the present invention showed a total grinding amount by from 1.3 to 1.8 times as much as that of the coated abrasive using a trace grade abrasive grain described in Japanese Patent Publication JP-A-60-231462 according to Comparative Example 21 in the case where the material to be ground was cold press steel plate SPC as will be understood from Table 10, and also showed a total grinding amount by even from 5.4 to 5.7 times as much as that of the conventional product in the case where the material to be ground was stainless steel SUS-304 as will be understood from Table 11.

CLAIMS

1. An α -alumina-based ceramics material comprising crystals of a particle diameter of no greater than $0.2\ \mu\text{m}$ on an average or a particle diameter of substantially no greater than $0.2\ \mu\text{m}$, and having a density of no lower than 95% of a theoretical density and a Vickers hardness of no lower than $2,000\ \text{kg/mm}^2$.

2. An alumina-based abrasive grain comprising said ceramics material described in Claim 1.

3. A grinding wheel or coated abrasive using said alumina-based abrasive grain described in Claim 2.

4. A ceramics material as described in Claim 1, wherein said ceramics material contains no more than 20 wt% of at least one member of oxides of Fe, Cu, Ni, Ba, Be, Mg, Cr, Si, Mn, Zr, Ti, Ca, V, Ga and Rh.

5. An alumina-based abrasive grain comprising said ceramics material described in Claim 4.

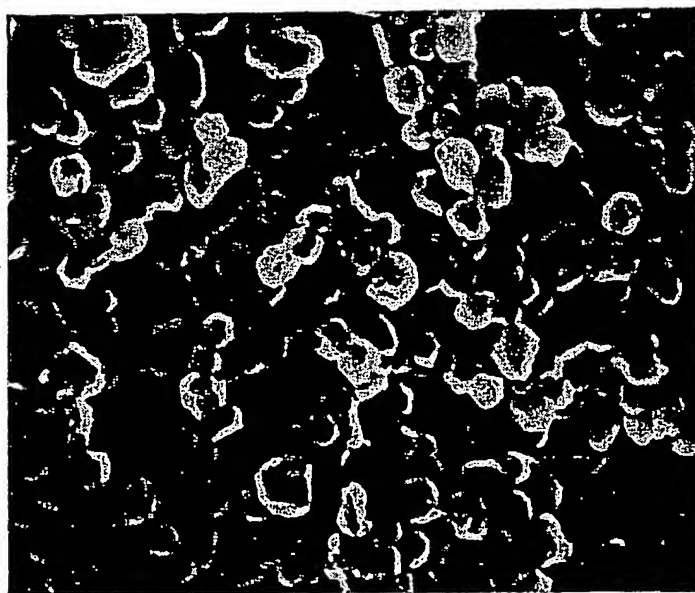
6. A grinding wheel or coated abrasive using said alumina-based abrasive grain described in Claim 5.

temperature in a range of from 1,100 to 1,300°C for from 30 seconds to 10 minutes and further retaining it at a temperature of from 1,000 to 1,200°C for 1 to 100 hours.

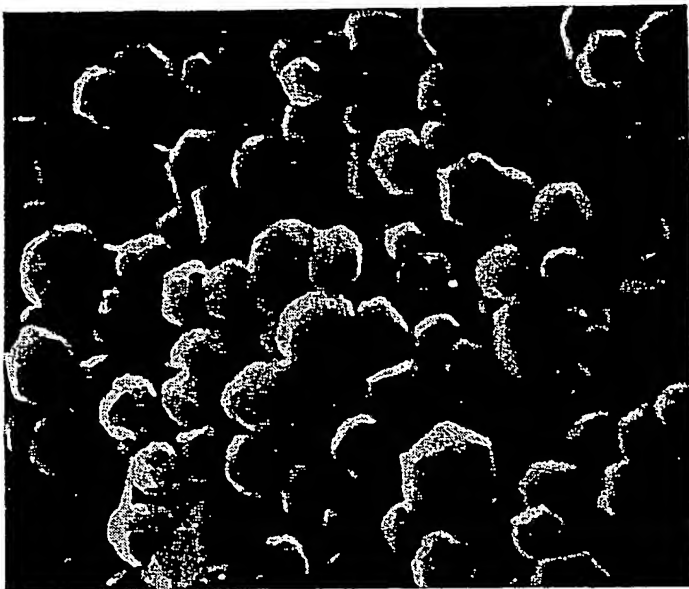
10. A method as described in Claim 9, wherein said ceramics material contains in said ceramics material at least one member of oxides of Fe, Cu, Ni, Ba, Be, Mg, Cr, Si, Mn, Zr, Ti, Ca, V, Ga and Rh, and precursors thereof in an amount of no more than 20 wt% in terms of oxide.

11 10 90

Fig. 2



Example 2



Comparative Example 1